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Overview of Impacts on Drinking Water Quality

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DISINFECTANT CHEMISTRY IN DRINKING WATER - OVERVIEW OF IMPACTS ON DRINKING WATER QUALITY

by

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DISINFECTANT CHEMISTRY IN DRINKING WATER - OVERVIEW OF IMPACTS ON DRINKING WATER QUALITY

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ABSTRACT

Chemicals commonly considered for use as disinfectants in municipal drinking water treatment are chlorine, chloramines, chlorine dioxide, and ozone. Considerations such as disinfection power, ease of application, and low cost have led in the past to the use of free chlorine ($HOCl/OCl^-$) as the primary disinfectant. Discovery of trihalomethanes, formed by the action of free chlorine upon natural organic materials such as aquatic humic materials, has led to a reexamination of this practice. In many cases a change to an alternative disinfection practice has either occurred or is being contemplated by utilities that otherwise have difficulty meeting the maximum contaminant level requirement for trihalomethanes. Chloramines, chlorine dioxide, or ozone when used alone do not usually cause significant formation of trihalomethanes. Each is an active oxidant, however, and has the potential of forming objectionable byproducts other than trihalomethanes (as may chlorine as well). Free chlorine, for example, forms "organic halogen" substantially in excess of that accounted for by the trihalomethanes. Chloramines and chlorine dioxide do also, although less than free chlorine. Specific reaction products of each in aqueous solution are now being identified. Thus, the beneficial use of each of these chemicals as a biocide in drinking water treatment may have its own less desirable side effects.

When we were first asked to present a paper at this Symposium on the subject of disinfectant chemistry in drinking water as an "overview" paper, we had in mind a somewhat traditional textbook approach discribing in a brief way all the known basic chemistry. After reminding ourselves of the complexity of that, including the problem of distilling the huge volume of literature on that subject, we decided to take a different approach that we think is more appropriate for this group and better addresses the thrust of this symposium. That is, we plan to address the various perceived impacts of the application of disinfectant chemicals on drinking water quality in a comparative way and, to the extent it is understood, to relate these observations to the known chemistry of each disinfectant. The basic chemistry of the oxidants in water treatment, uses as oxidants, as disinfectants, and of trihalomethane formation and control have been reviewed in a much more complete and detailed fashion elsewhere[1-5], and this material served as the source of much of the following discussion.

DISINFECTANTS

Four chemical oxidants are most often considered as drinking water disinfectants. These are chlorine (free), chloramines ("combined chlorine"), chlorine dioxide, and ozone.

Free Chlorine

Free chlorine exists in aqueous solution as a mixture of hypochlorous acid (HOCl) and hypochlorite (OCl^-) ion:

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^- \qquad (1)$$

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (2)$$

The source can be chlorine gas or a hypochlorite preparation such as NaOCl (solution) or $Ca(OCl)_2$. In either case, the final pH of the drinking water establishes the relative amounts of each of the active species. At pH 7.5 the two exist in almost equal concentrations.

Chloramines

The chemistry of "combined chlorine" is essentially the combined chemistries of free chlorine and ammonia. The ammonia may be present naturally in the source water or added intentionally by the utility.

Free chlorine first reacts with ammonia (NH_3) to form monochloramine (NH_2Cl) by the substitution reaction:

$$HOCl + NH_3 \rightleftharpoons NH_2Cl + H_2O \qquad (3)$$

Sequential reactions occur to form dichloramine ($NHCl_2$) and nitrogen trichloride (NCl_3). Oxidation occurs in the process when sufficient chlorine excess is present to remove the ammonia as nitrogen gas:

$$2NHCl_2 + H_2O \longrightarrow N_2 + HOCl + 3H^+ + 3Cl^- \qquad (4)$$

All of this is somewhat simplified, and the end result is heavily dependent on pH. Nevertheless, for the purposes of this paper it is sufficient to understand that free chlorine exists only in very small quantity (relative to that added) until the ammonia is decomposed and removed as nitrogen gas by the process well known in the drinking water industry as breakpoint chlorination (Figure 1).

Chlorine Dioxide

Chlorine dioxide (ClO_2) is a gas at normal temperatures and pressure and exists as molecular ClO_2 in pure aqueous solution. Pure chlorine dioxide is unstable and can be an explosive mixture in air at approximately eleven percent.[4] For that reason it is produced on-site at a utility. This is usually by reaction of sodium chlorite with excess chlorine in acid solution:

$$HOCl + H^+ + 2ClO_2^- \longrightarrow 2ClO_2 + H_2O + Cl^- \quad (5)$$

Although disproportionation of ClO_2 to form ClO_2^- and ClO_3^- takes place, this reaction is much slower and, therefore, is less important from a chemical disinfectant standpoint than the nearly immediate hydrolysis of molecular chlorine to hypochlorite. Chlorine dioxide does not react with ammonia, but ammonia-free waters do exhibit a demand for ClO_2 similar in magnitude to that for free chlorine.[3]

Ozone

Molecular ozone (O_3) is a very strong oxidant and relative to the above disinfectants has a very short half life in water - said to be on the order of twenty minutes at low pH values. Molecular ozone is the reactive species at neutral and lower pH values, reacting through an ionic mechanism. At pH values above 8-9, O_3 reacts with water to produce hydroxyl and hydroperoxide radicals as the active species.[4]

Relative disinfection effectiveness

The primary reason for the use of disinfectants in the treatment of drinking water is to ensure the destruction of pathogenic microorganisms during the treatment process, thereby preventing the transmission of disease by drinking water. Secondarily, the presence of a disinfectant in the water distribution system helps to maintain the quality of water by preventing the growth of nuisance microorganisms.

The effectivess or efficiency of biocidal agents is determined by the rate at which the reaction or killing of the microorganism population proceeds.[3] The comparative biocidal efficiencies of disinfectants are frequently expressed as the relative concentration (mg/L) of different disinfectants needed to obtain equivalent disinfection rates, or as the

relative inactivation rates produced by the same concentration of different disinfecting agents. Most of this information has been obtained by laboratory experimentation under carefully controlled conditions, which include clean systems, the absence of extraneous disinfectant-demanding substances, and the use of pure cultures of the microorganism under study. The presence (in solution) of materials exerting disinfectant demand is likely to change disinfection efficiencies by way of competing reaction mechanisms. This effect complicates extrapolations from experiments with clean systems to expected water utility performance. Nevertheless, comparisons of disinfectant performance under laboratory conditions are instructive.

Data from the results of a number of experiments conducted using different disinfectants at various concentrations can be used to construct plots of the type shown in Figure 2. These results show the exposure times and concentrations of several disinfectants needed to produce a given level of inactivation of a given microorganism. The results show that chlorine dioxide at pH 7 and HOCl at pH 6 produce similar rates of inactivation of Escherichia coli. Hypochlorite ion (OCl^-) at pH 10 was less effective, and monochloramine at pH 7 and dichloramine at pH 4.5 were even less so. A similar plot showing virucidal efficency of these disinfectants for poliovirus 1 is shown in Figure 3. Note that higher disinfectant concentrations and longer contact times in general are needed for inactivation of poliovirus 1 than for E. coli.

A comparison of the relative positions of the curves on Figures 2 and 3 reveals that the relative efficencies of the various disinfectants vary according to the target organism. Ozone is not included in these Figures

because fast reaction rates and disinfectant instability causes limitations on sampling times and ozone measurements to make good experimental results difficult to obtain. Ozone does, however, inactivate microorganisms at a high rate.

Assessing the efficiencies of different free and combined chlorine species also is complicated by the nature of the chemical reactions that determine the chemical species present and the chemical equilibria established under various pH conditions. For instance, during the reaction of equation (2) a rapidly achieved equilibrium exists that is drastically influenced by pH. At pH 10 approximately 0.5 percent of the free residual chlorine is still present as HOCl, and because it is a much more powerful biocide than OCl^-, its presence could substantially influence the biocidal activity observed.

Similarly, equation (3) is reversible, and a solution of 2 mg/L NH_2Cl is estimated to be 0.58 percent hydrolyzed (0.58 percent HOCl) at pH 7 and 25°C. Because of the much higher biocidal efficiency of HOCl, its influence on the disinfection rate observed could be substantial and could explain the influence of pH on the biocidal efficiency of monochloramine.

Furthermore, equation (6)

$$H^+ + 2NH_2Cl \rightleftharpoons NH_4^+ + NHCl_2 \qquad (6)$$

indicates that although mostly monochloramine is formed when excess ammonia is present at high pH (>8), addition of hydrogen ion (lowering pH) will cause formation of dichloramine, with the position of this equilibrium being determined by the pH of the treated water. Thus with chlorine and chloramines, pure species are never present, and pH determines which are present and their proportions. The influence of pH, therefore, cannot be experimentally separated from species effectiveness for disinfection.

Nevertheless, in the case of chlorine, disinfection efficiency declines rapidly as the pH is increased from 7 to 9. The efficiency of chlorine dioxide also changes substantially over this pH range; but in contrast to chlorine, the effectiveness increases as the pH increases (Figure 4). In this case, the change appears to be in microorganism sensitivity rather than in disinfectant species present because, unlike chlorine, chlorine dioxide does not so rapidly dissociate or disproportionate into different chemical species within this pH range.

The pH of the water also affects ozone chemistry. At high pH values, ozone decay is accelerated, proceeding through radical ion intermediates (see above); thus, the pH of the water being treated may also influence ozone effectiveness.

Other Beneficial Uses

Although the primary purpose of adding these oxidants to drinking water during treatment is for the control of microbiological contaminants, especially pathogenic organisms, certain side benefits also accrue.[1-5] Source waters high in ferrous iron and manganese are successfully treated with ClO_2, O_3, and free chlorine by oxidative precipitation. Ozone has been observed to improve the clarification process. Chlorine can remove ammonia, and hydraulics are improved or maintained by control of slimes and macroorganisms. Ozone and chlorine dioxide are used to remove or prevent taste and odor. In some locations the oxidants are used to remove color, and it is this latter case that hints of the occurrence of some less desirable side effects.

Negative Aspects of Disinfectant Use

Many considerations such as disinfection power, ease of application, and low cost have led in the past to the heavy use of free chlorine

($HOCl/OCl^-$) as the primary disinfectant in drinking water treatment, often very early in the treatment process. Discovery of trihalomethanes, however, formed by the action of free chlorine upon natural organic material, including aquatic humic materials that are responsible for undesirable color in many source waters, has led to a reexamination of this practice.

Although sporadic reports of the presence of chloroform and other trihalomethanes in finished drinking water occurred before 1974, the reports that year by Rook[8] of the Rotterdam Water Utility in The Netherlands and by Bellar, Lichtenberg, and Kroner[9] of U.S. Enivronmental Protection Agency (USEPA) clearly demonstrated that these contaminants were formed during the water treatment process as a result of chlorination. This finding prompted a survey[10] in early 1975 of 80 water utilities in the United States, 79 of which practiced free residual chlorination or combined residual chlorination. This survey, the National Organics Reconnaissance Survey (NORS), showed that all of the water utilities that used free chlorine in their treatment practice had varying concentrations of at least one of four trihalomethanes in their finished drinking water and that they were formed during treatment. Follow-up studies in 1975-1977, including the National Organics Monitoring Survey,[11] supported these conculsions with analysis of samples collected at 113 locations during three different seasons.

These surveys, combined with like results from all over the world, showed that the reaction of chlorine to produce trihalomethanes was widespread and surely had been occurring for as long as chlorine had been in use in water treatment. Since the discovery of trihalomethanes in drinking water, a very large effort has focused on gaining an understanding of natural factors that influence the formation of trihalomethanes and would lead to means for their control during drinking water treatment.

The four trihalomethanes most commonly found in finished drinking water are chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$). A fifth, dichloroiodomethane ($CHCl_2I$) is found much less frequently. A source of organic precursors that reacts with chlorine is generally accepted to be aquatic humic materials found in virtually all drinking water sources, especially surface supplies. These humic materials include both humic- and fulvic acids that when present in high concentration, account for much of the color in those waters. Natural bromide and iodide are considered responsible for the non-chlorine halogens.

Trihalomethanes from Chlorination

The concentrations of trihalomethanes observed in water treatment and distribution are heavily dependent on reaction time, humic material concentration, pH, temperature, and to a smaller extent, chlorine dose/residual.[3] Formation is strongly dependent on chlorine dose when the reaction is chlorine limited, but little change can be seen in $CHCl_3$ concentration once the demand requirement has been met and the residual maintained as in the example shown (Figure 5).

Bromide ion, even at very low concentrations relative to the applied chlorine, strongly influences the mixture of trihalomethanes formed (Figure 6). This occurs as a result of rapid oxidation of Br^- to HOBr followed by reaction of this active species with the organic precursor. The reaction of bromine with humic substances is much more rapid than that of chlorine resulting in both the disproportionate share of bromine-containing species and approaching a final trihalomethane concentration much earlier (usually minutes rather than hours or days).

After much study of treatment feasibility and careful consideration of potential health effects, the USEPA promulgated a Regulation on November 29, 1979 limiting concentrations of total trihalomethanes ($CHCl_3$ + $CHCl_2Br$ + $CHClBr_2$ + $CHBr_3$) to 0.10 mg/L at utilities serving populations greater than 10,000 population.[13] This Regulation becomes effective over a four year schedule and has caused many utilities to reexamine their treatment processes including approach to disinfection. In many cases a change to an alternative disinfection practice has either occurred or is being contemplated by utilities that otherwise have difficulty meeting the maximum contaminant level requirement for trihalomethanes in drinking water.

Alternative Disinfectants and Trihalomethane Formation

Preformed chloramines do not produce trihalomethanes.[3] Generally, the addition of ammonia will stop the formation of trihalomethanes. Exceptions to this have been observed, and one possible explanation is that intermediates built-up during the chlorination step are hydrolyzed after the free chlorine is removed with ammonia. The presence of bromide can also cause the reaction to approach completion before the NH_3 is added, reducing the effectiveness of NH_3 as a control measure.

Chlorine dioxide used alone also does not generally form trihalomethanes,[14,15] although in one instance trihalomethane formation has been reported at pH 12, very high for drinking water treatment practice.[16] Additionally, chlorine dioxide plus excess chlorine actually results in lower final trihalomethane concentrations than the same amount of chlorine alone.[3,14]

Ozone alone does not form trihalomethanes except possibly in the presence of excessive bromide ion.[3,4] Ozone can influence the yield of

trihalomethanes, either upward or downward, resulting from subsequent chlorination of the ozone treated water necessary to maintain a disinfectant residual in the distribution system.[3]

Other Reactions

The literature is filled with ample evidence that the active oxidants are sufficiently reactive with organic compounds that byproduct formation might be expected.[1-5] For example, the formation of chlorophenols by chlorine accompanied by the associated odor problems has long been known in the drinking water field. This can be prevented by chlorine dioxide use even though chlorophenols can be formed under certain conditions (Table I) and indicates a different kind of reactivity of ClO_2. As mentioned before, ozone is a very reactive compound and has a very short half life. Ozone is well known by chemists engaged in organic synthesis to readily react with organic compounds of certain classes. Chloramines, much less reactive than chlorine, persist for long periods in treated water and are probably less prone to produce identifiable byproducts. The reactions of all of these oxidants with aquatic humic materials is only beginning to be understood, however, primarily because of the complexity and relatively uncharacterized nature of the substrate material itself. Much of this is non-volatile, high molecular weight material that cannot be identified or measured by gas chromatographic techniques.[17] Many of the expected byproducts would be expected to fall within this category as well.

TABLE 1. PRODUCTS RESULTING FROM CHLORINE DIOXIDE TREATMENT OF PHENOL[15]

ClO_2/phenol (mole/)(mole[b])	Yield from Phenol, %[a] o-Chlorophenol	Phenol recovered	2,4-Dichlorophenol	p-Chlorophenol	p-Hydroquinone	Total Recovery
4/5	11	30	0.3	13	3.6	58
14/5	NF[c]	NF	NF	NF	7.2	7.2
14/1	NF	NF	NF	NF	45	45

[a]Reaction time, 4 hr.
[b]In mg/L., 4/5 = 43.5/75; 14/5 = 150/75; 14/1 = 164/16.
[c]None found.

Total Organic Halogen

One approach to characterizing and quantifying byproduct formation from the disinfectants that contain halogen is to measure Total Organic Halogen (TOX) which can be done by use of an activated carbon adsorption-pyrolysis technique.[18] In our laboratory, this analytical technology was applied, with appropriate control solutions, to solutions of a soil humic acid that was treated separately with each of the three disinfectants: free chlorine, combined chlorine (chloramines), and chlorine dioxide. Time, temperature, pH, disinfectant dose, and organic substrate concentrations were varied. Selected examples of the results obtained are presented in Figures 7 and 8.

The bar graphs in Figure 7 represent Non-Purgeable Organic Halogen (NPOX) above the zero line and Purgeable Organic Halogen (POX), measured as trihalomethanes (in this case exclusively $CHCl_3$), below the zero line. The full length of a bar, therefore, represents

Total Organic Halogen (TOX). Arranged in this manner, the concentration of TOX in solution at 20°C can be seen to be mostly composed of NPOX at pH values of 5 and 7, while at pH 11 the amount of trihalomethanes present is the greater. The ratio of NPOX to trihalomethanes is shown to diminish with increasing pH, which occurs because increasing pH favors a slight increase in trihalomethane formation while at the same time promoting a drastic decrease in NPOX concentration.

The effect on organic halide formation of increasing the dose of chlorine from 8.1 mg/L to 20 mg/L at 20°C is also demonstrated in Figure 7. Compared with the low dose, TOX is increased by 29, 36 and 27% at pH values near 5, 7 and 11, respectively, at the higher dose. This is due almost entirely to an increase in NPOX formation.

Figure 7 also reveals a relatively rapid formation of NPOX within the first two hours after dosing with chlorine when compared to THM formation. All of these results of chlorination are typical of those reported for humic materials from other sources (Fleischacker and Randke).[19]

Figure 8 compares the NPOX and trihalomethane formation at 20°C at 3 different pH levels for each of the three disinfectants, chlorine, chloramines and chlorine dioxide. NPOX formation is reduced by 85% when comparing the use of chloramine as the disinfectant to chlorine and is even much lower when chlorine dioxide is used. Trihalomethane formation is reduced by greater than 95% when chloramines were used, and no trihalomethanes were detected when chlorine dioxide was used. Unlike with chlorine, which increases the formation of trihalomethanes with increasing pH, the use of chloramines and chlorine dioxide as disinfectants results in a decrease in the formation of all organic halides with increasing pH. NPOX formation with chlorine dioxide was rapid with no difference observed between 2 hr and 144 hr sample concentrations.

As part of the above studies, these tests were also run at three temperatures (4, 20 and 36°C) and the general effect of increasing temperatures was to produce more total organic halide whatever the disinfectant used and regardless of the pH. The most significant increase in TOX was always encountered at pH near 5 and was primarily due to an increase in NPOX. In a similar set of tests that involved a lowering of organic substrate concentration from 5 mg/L to 2 mg/L and an increase in chlorine concentration from 8.1 to 10 mg/L, TOX formation was reduced by 55%. A reduction in both THM and NPOX formation occurred in this test.

Thus, the evidence from varying chlorine disinfectant concentration and organic substrate concentration indicates that at any given pH and temperature, THM formation increases principally as a function of organic substrate concentration, and NPOX formation increases as a function of both organic substrate concentration and chlorine concentration.

Other Specific Compounds Produced

Specific compounds that account for a share of the observed byproducts comprising the total organic halogen other than trihalomethanes are being found. These include dihaloacetonitriles and mono-, di-, and trichloroacetic acids. Numerous other compounds, some containing chlorine, have been identified with relatively confident structural assignment.[20,21] For the most part, however this work has involved experiments designed to maximize byproduct yield, rather than mimic the drinking water treatment practice. Part of this work is the subject of a paper to be presented later this afternoon by Norwood.[22]

Figure 9 shows computerized reconstructions of fused silica capillary column gas chromatography/mass spectrometry data from 13 L of unchlorinated and 10 L of chlorinated (20 mg/L Cl_2) solutions of a soil humic acid

(5.3 mg/L TOC). In studies in our laboratory (unpublished) the samples were concentrated on granular activated carbon, extracted with ethyl ether, and methylated with diazomethane. Forty nanograms of 1-chlorododecane was injected with each sample, and each chromatogram has been adjusted for a 100 percent response for the internal standard. This example graphically illustrates in a qualitative way[17] the chromatographable byproducts produced by the addition of chlorine to this sample.

Similar earlier studies in our laboratory, using XAD-8 resin to concentrate the chlorination byproducts attempted to compare the same soil humic acid with an aquatic humic acid and a finished water from a surface water with a relatively low humic material concentration. The soil humic acid experiment was performed twice to check the reproducibility of the methodology, and approximately twice the volume of tap water was concentrated because of the low humic material concentration. Both mass spectral data and chromatographic retention time data were used to check for recurrence of individual compounds. Actual identification was not attempted in most cases, and most spectra did not match available reference spectra. Designation of a peak as chlorinated was based on visual inspection of mass spectral data for characteristic ion clusters.

Table 2 lists the numbers of chlorination byproducts (unique retention time and spectra), both chlorinated and nonchlorinated, from various humic materials; trihalomethanes and compounds also found in the nonchlorinated samples or solvent blanks are not included in the list. Of all the compounds detected in the three samples, the soil humic acid produced the most byproducts, especially chlorinated compounds. The aquatic humic acid produced approximately half as many as the soil, and the finished tap water data

indicated that, if produced from this source, relatively few of the by-products are surviving the treatment process. The soil humic acid had the largest number of byproducts that were not found in the other samples. In contrast, only three compounds were unique to the tap water sample indicating that those that did form were typical of aquatic humic material by-products.

TABLE 2

BYPRODUCTS FOUND FROM CHLORINATION OF DIFFERENT TYPES OF HUMIC ACID SOURCES

	Number of Compounds Found	
	Chlorine-containing	Nonchlorine containing
Total Unique Compounds (All Samples)	47	51
Soil Humic Acid	43	37
Aquatic Humic Acid	27	24
Finished Water	8	17
Unique to Soil Humic Acid	16	18
Unique to Aquatic Humic Acid	4	11
Unique to Finished Water	0	3

Inorganic End Products

Each of the active oxidants may produce reduced species or disproportionation products of concern. Free chlorine is mostly dissipated as chloride ion at a concentration insignificant relative to normal background.

When chlorine dioxide reacts with organic compounds the byproduct chlorite (ClO_2^-) is formed. Furthermore, as chlorine dioxide disproportionates in water, both chlorite and chlorate (ClO_3^-) are formed as byproducts. The relative proportion of these byproducts was determined during a study reported elsewhere by Miltner[23] in which 1.5 mg/L of chlorine dioxide was added to Ohio River water that had been treated in a pilot plant. The data in Table 3 show that approximately 50% of the original chlorine dioxide was converted to chlorite, about 25% to chlorate, and approximately 25% to chloride. Thus, when chlorine dioxide is used as an alternative disinfectant, the health significance of inorganic anions other than chloride must be considered. These inorganic byproducts are unique to chlorine dioxide.

TABLE 3

INORGANIC CHLORINE DIOXIDE BYPRODUCTS[a,14,23]

	Initial Concentration		Final Concentration		
Species	mg/L	mg/L as Cl^-	mg/L	mg/L as Cl^-	ClO_2 demand, %
ClO_2	1.5	0.8	0	0	-
ClO_2^-	-	-	0.7	0.4	50
ClO_3^-	-	-	0.4	0.2	25
Cl^-	17.9	17.9	18.1	18.1	25
Totals	-	18.7	-	18.7	100

[a] 1.5 mg/L ClO_2 added to Ohio River water which was coagulated, settled, dual-medial filtered. Contact time was 42 hr; pH was 7.1.

Chloramines themselves persist in a drinking water distribution system, and have been known to cause unique problems in kidney dialysis and to tropical fish.[3]

Summary

Considerations such as disinfection power, ease of application, and low cost have led in the past to the use of free chlorine ($HOCl/OCl^-$) as the primary disinfectant in drinking water treatment. Discovery of trihalomethanes, formed by the action of free chlorine upon natural organic materials such as aquatic humic materials, has led to a reexamination of this practice. In many cases a change to an alternative disinfection practice such as the use of chloramines, chlorine dioxide, or ozone has either occurred or is being contemplated by utilities that otherwise have difficulty meeting the maximum contaminant level requirement for trihalomethanes. These alternative disinfectants when used alone do not usually cause significant formation of trihalomethanes. Each is an active oxidant, however, and has the potential of forming objectionable byproducts other than trihalomethanes (as may chlorine as well). Free chlorine, for example, forms "organic halogen" substantially in excess of that accounted for by the trihalomethanes. Chloramines and chlorine dioxide do also, although less than free chlorine. Increasing numbers of specific reaction products of each disinfectant in aqueous solution are now being observed and some being identified. Thus, the benefical use of each of these chemicals as a biocide in drinking water treatment may have its own less desirable side effects.

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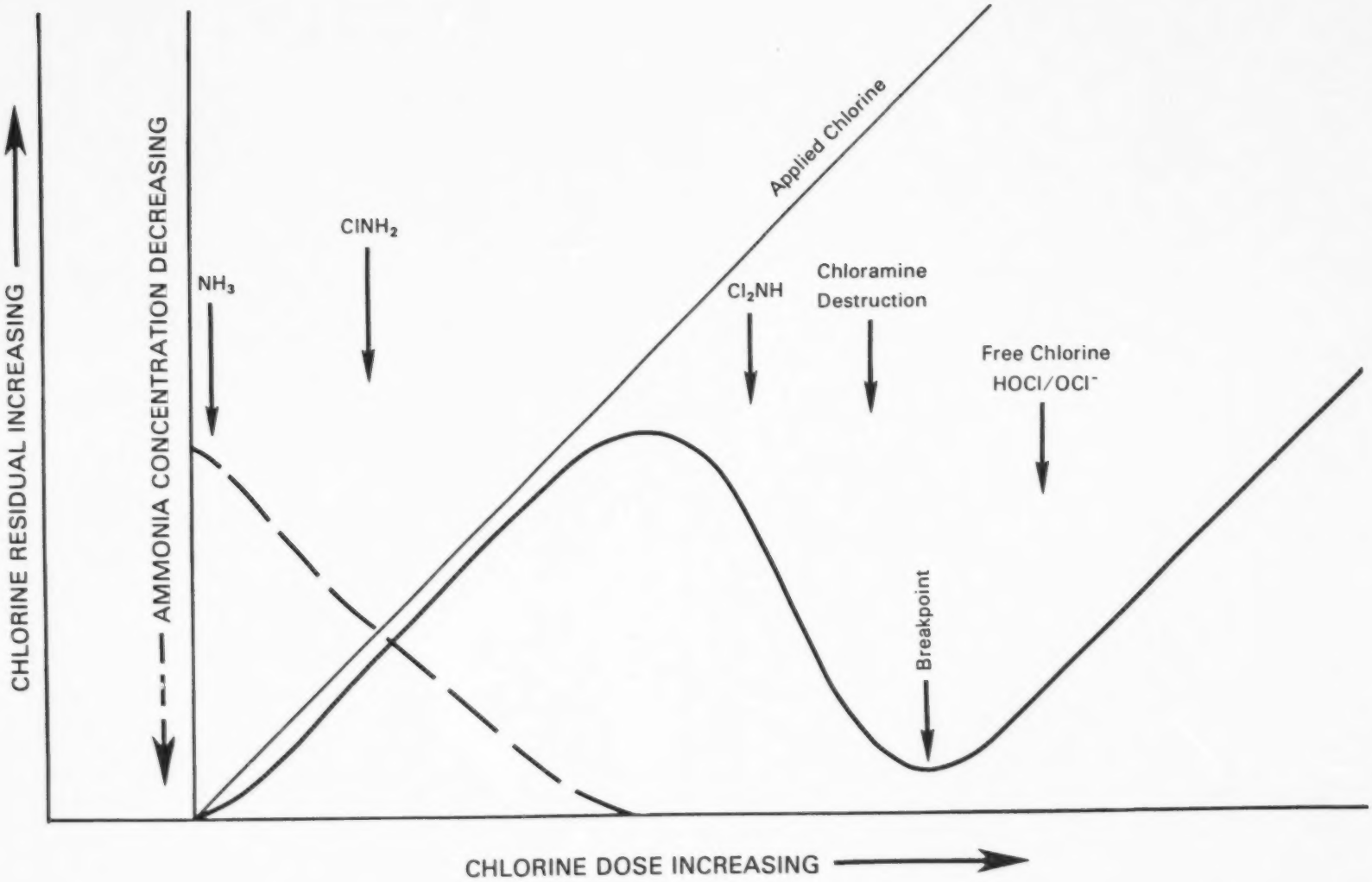

Figure 1. Chlorine - Ammonia Breakpoint Curve

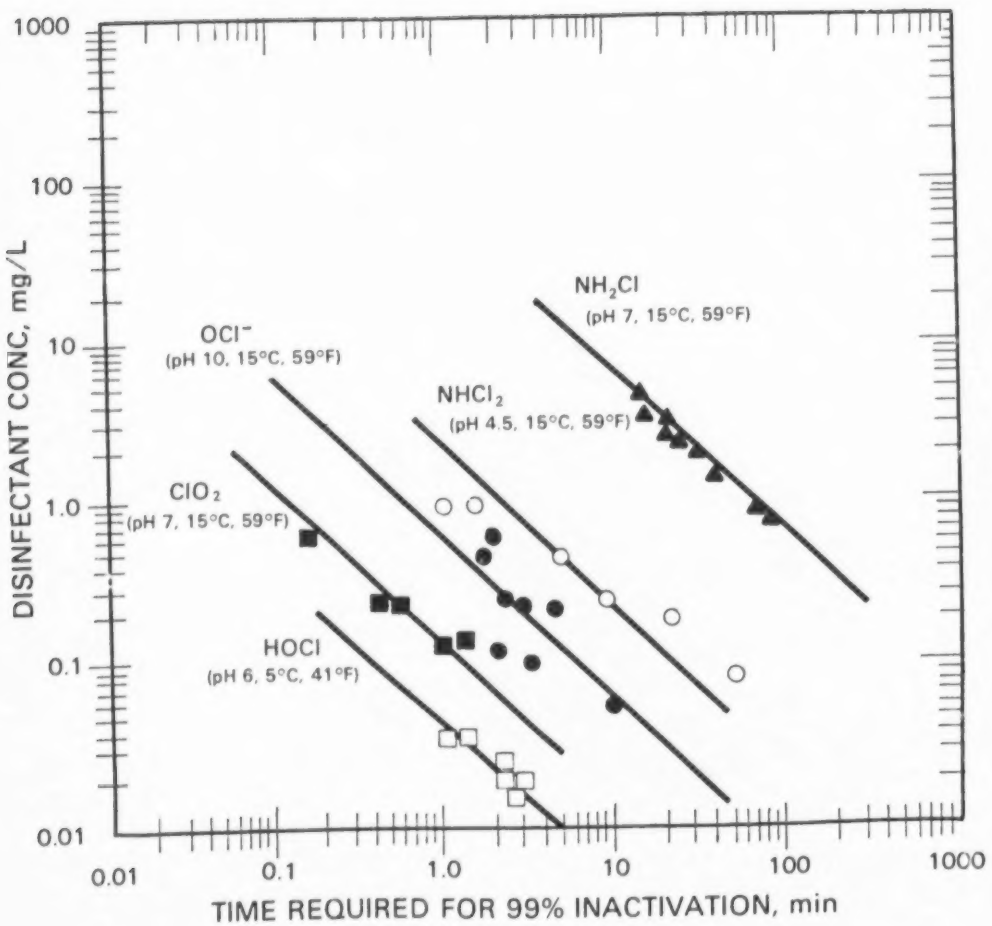

Figure 2. Inactivation of *E. Coli* (ATCC 11229)
(From Ref. 3, Based on Refs. 6, 7)

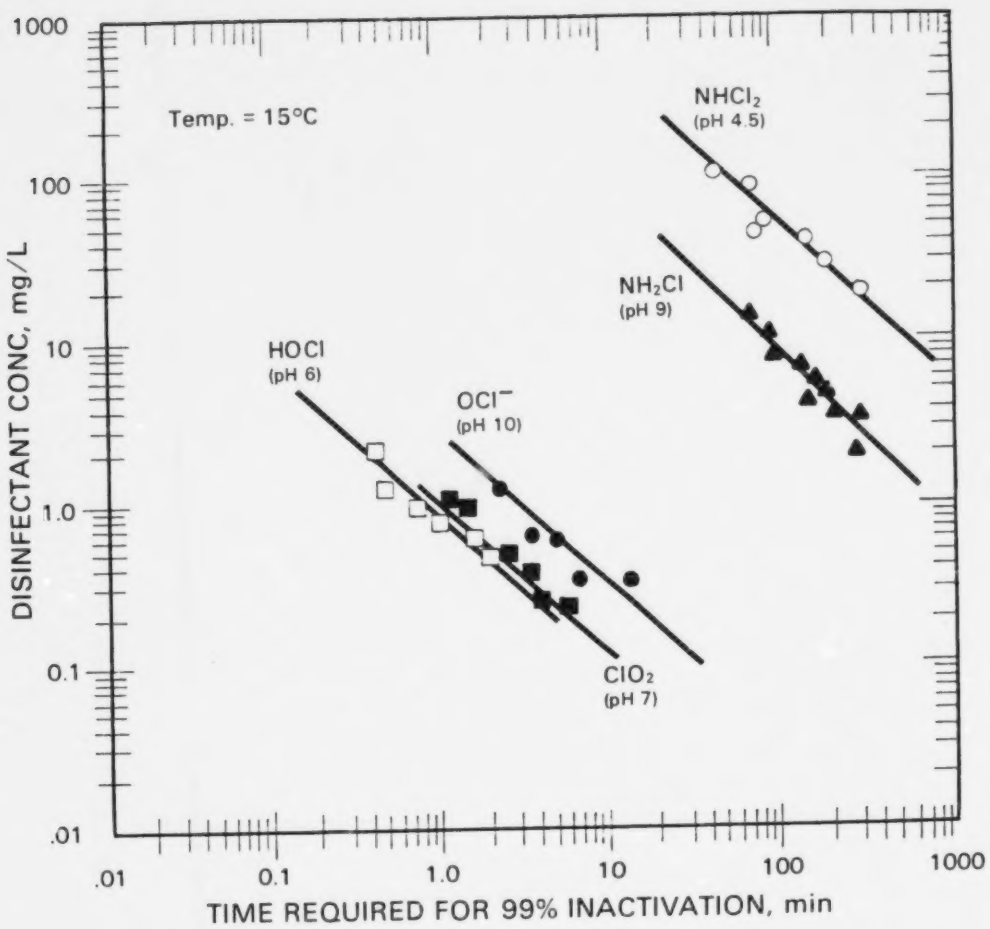

Figure 3. Inactivation of Poliovirus 1 (Mahoney)
(From Ref. 3, Based on Refs. 6, 7)

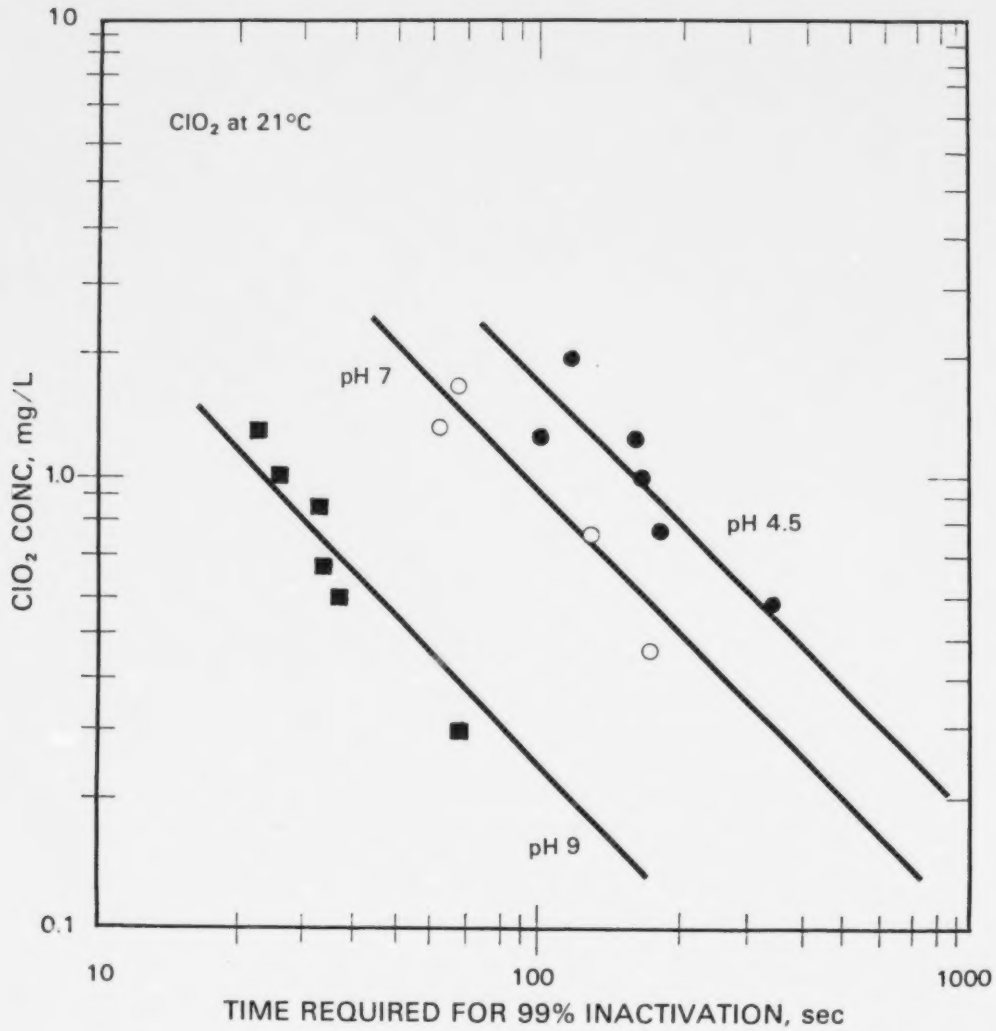

Figure 4. Effect of pH on Inactivation of Poliovirus 1 (Mahoney)
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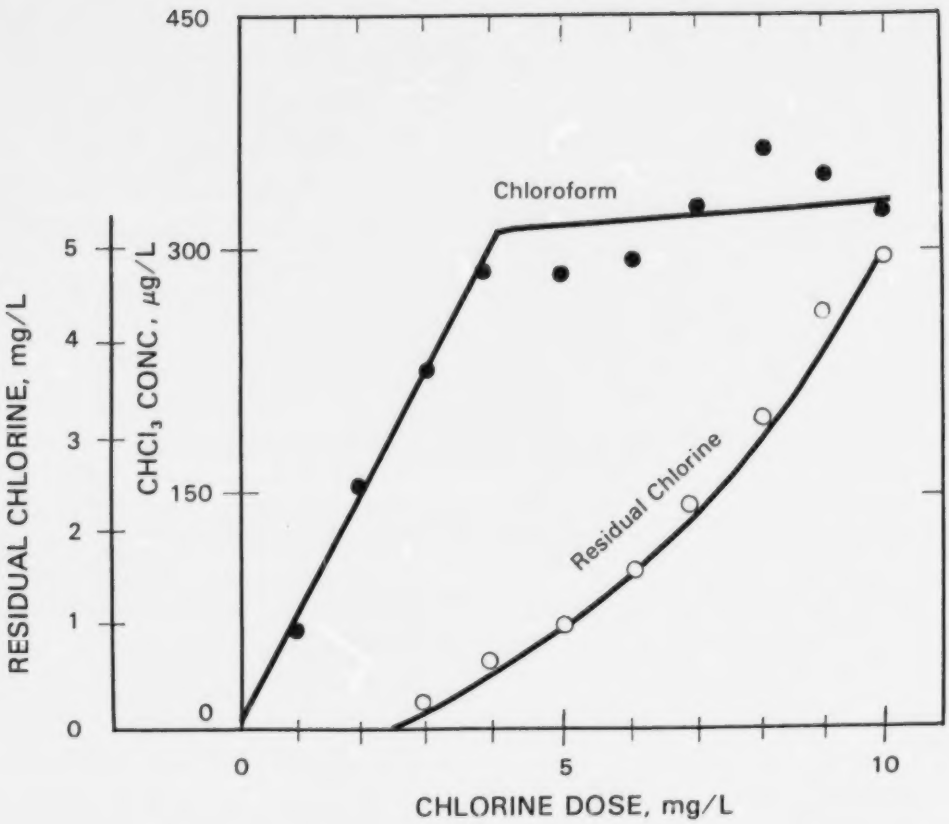

Figure 5. Chloroform Formation Compared with Chlorine Residual (From Ref. 3, Based on Ref. 12)

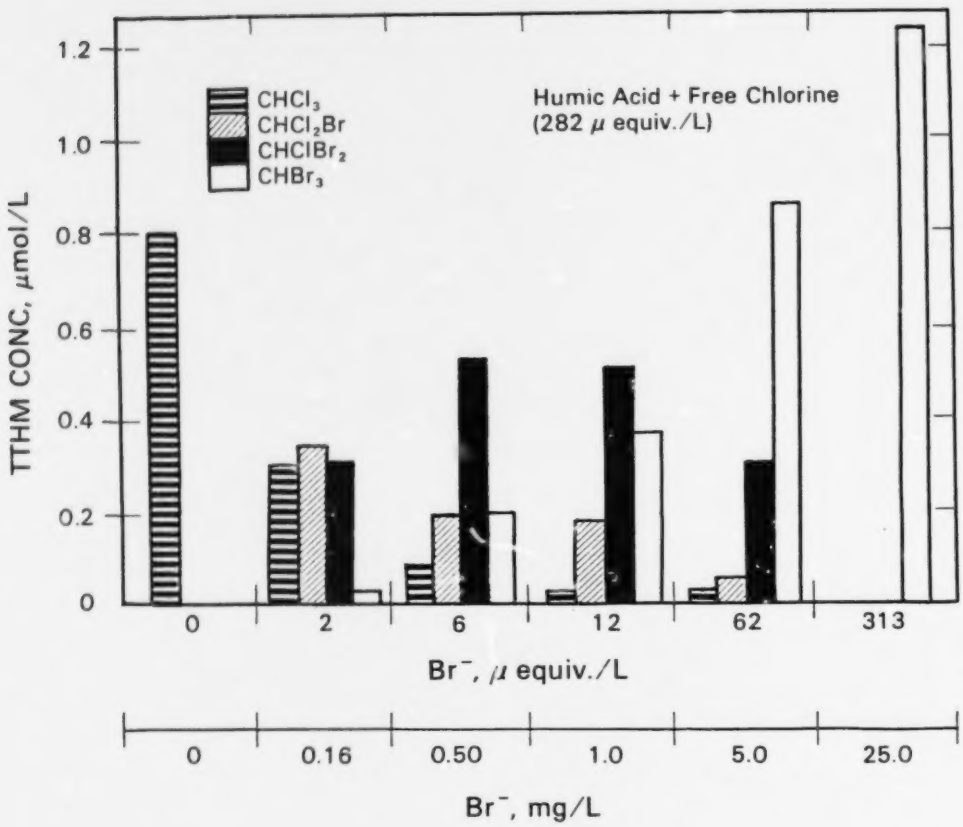

Figure 6. Distribution of Trihalomethanes with Varying Bromide Concentration (From Ref. 3)

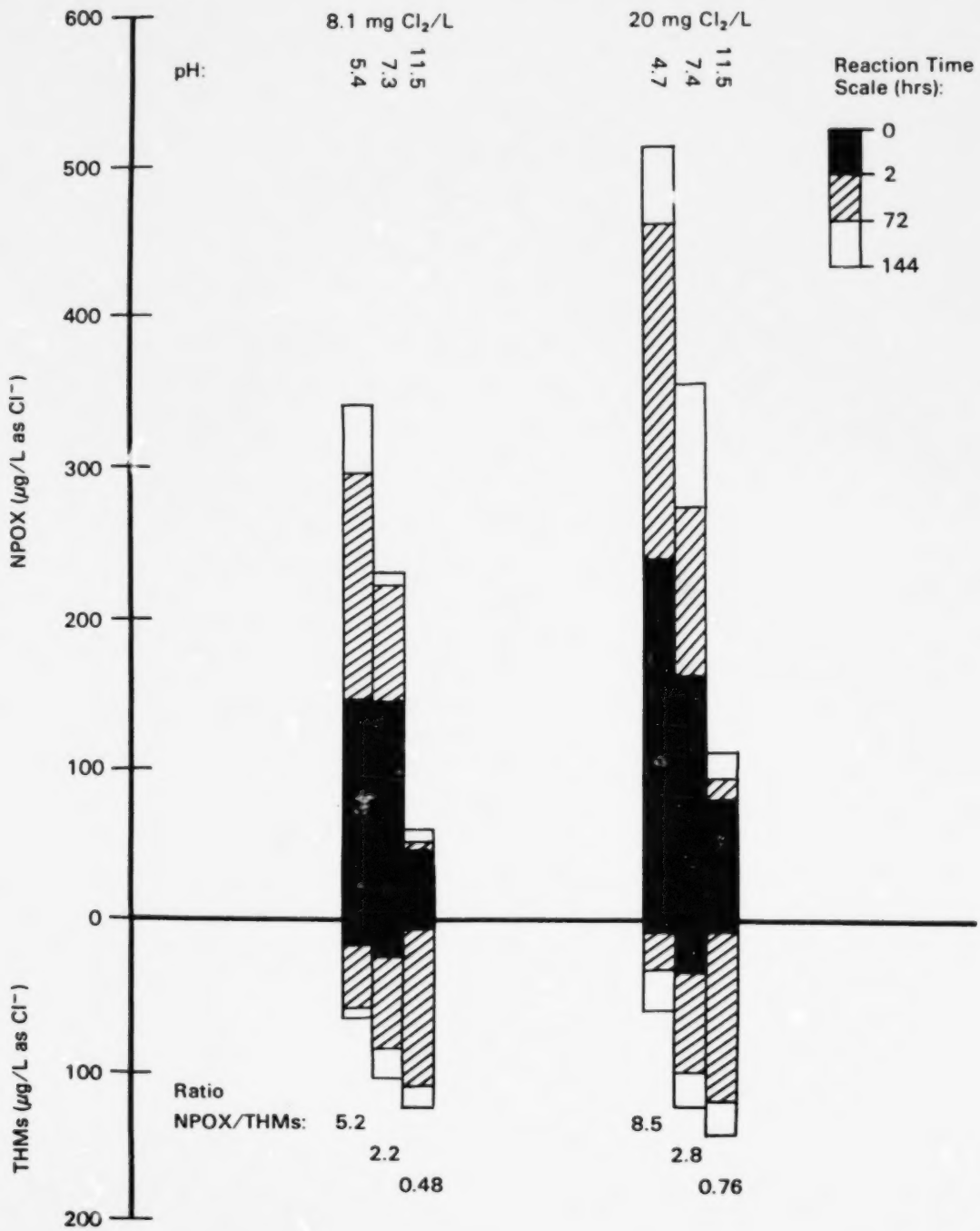

Figure 7. A Comparison of the Effects of pH and Oxidant Dose on the Formation of NPOX and THMs ($CHCl_3$) at 20°C in Distilled Water Solutions of 5mg Humic Acid/L. Note that THMs + NPOX = TOX (the entire bar).

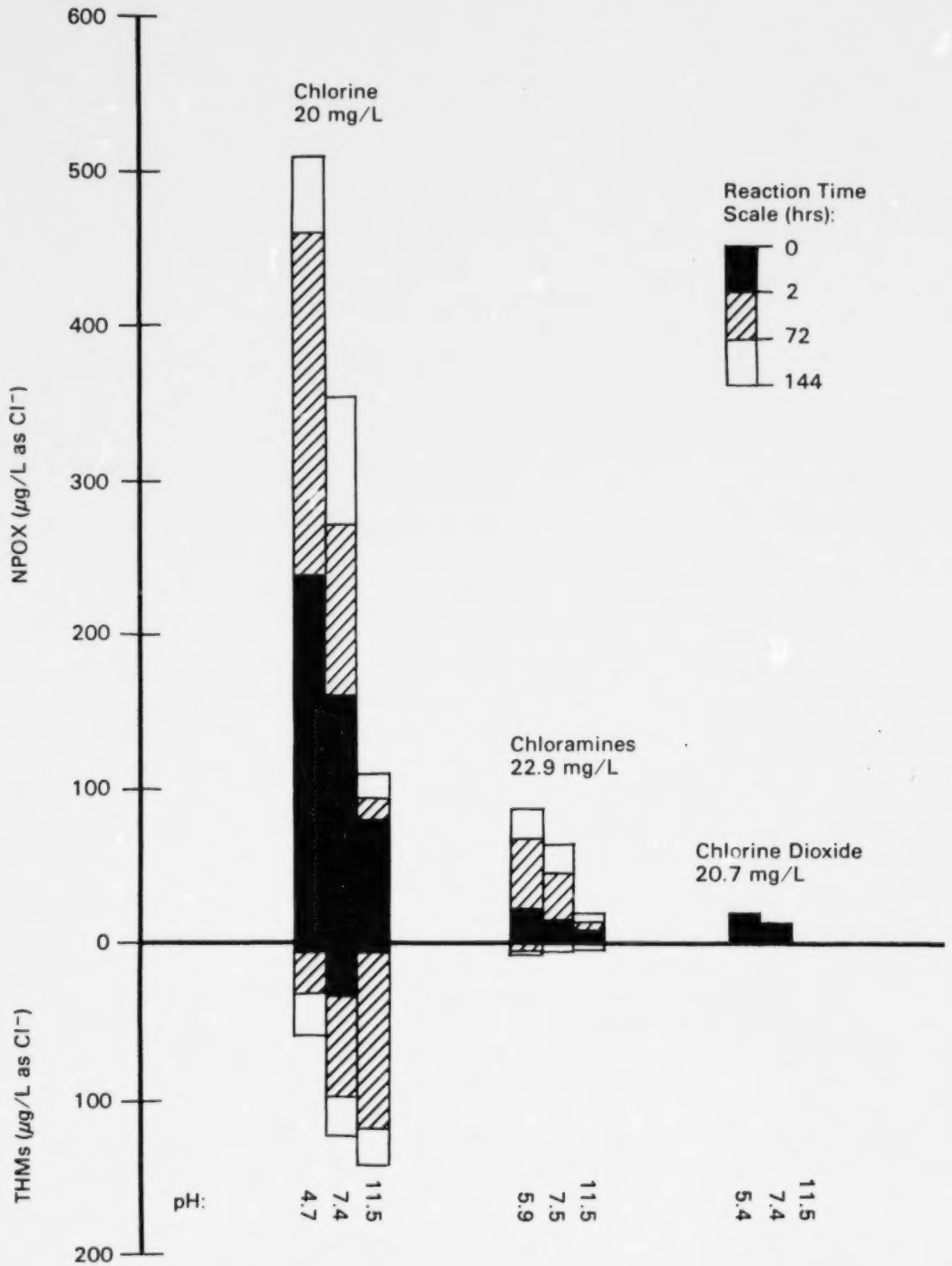

Figure 8. A Comparison of the Formation of NPOX and THMs ($CHCl_3$) at 20°C in Distilled Water Solutions of 5 mg Humic Acid/L Dosed with Various Disinfectants. Note that NPOX + THMs = TOX (the entire bar).

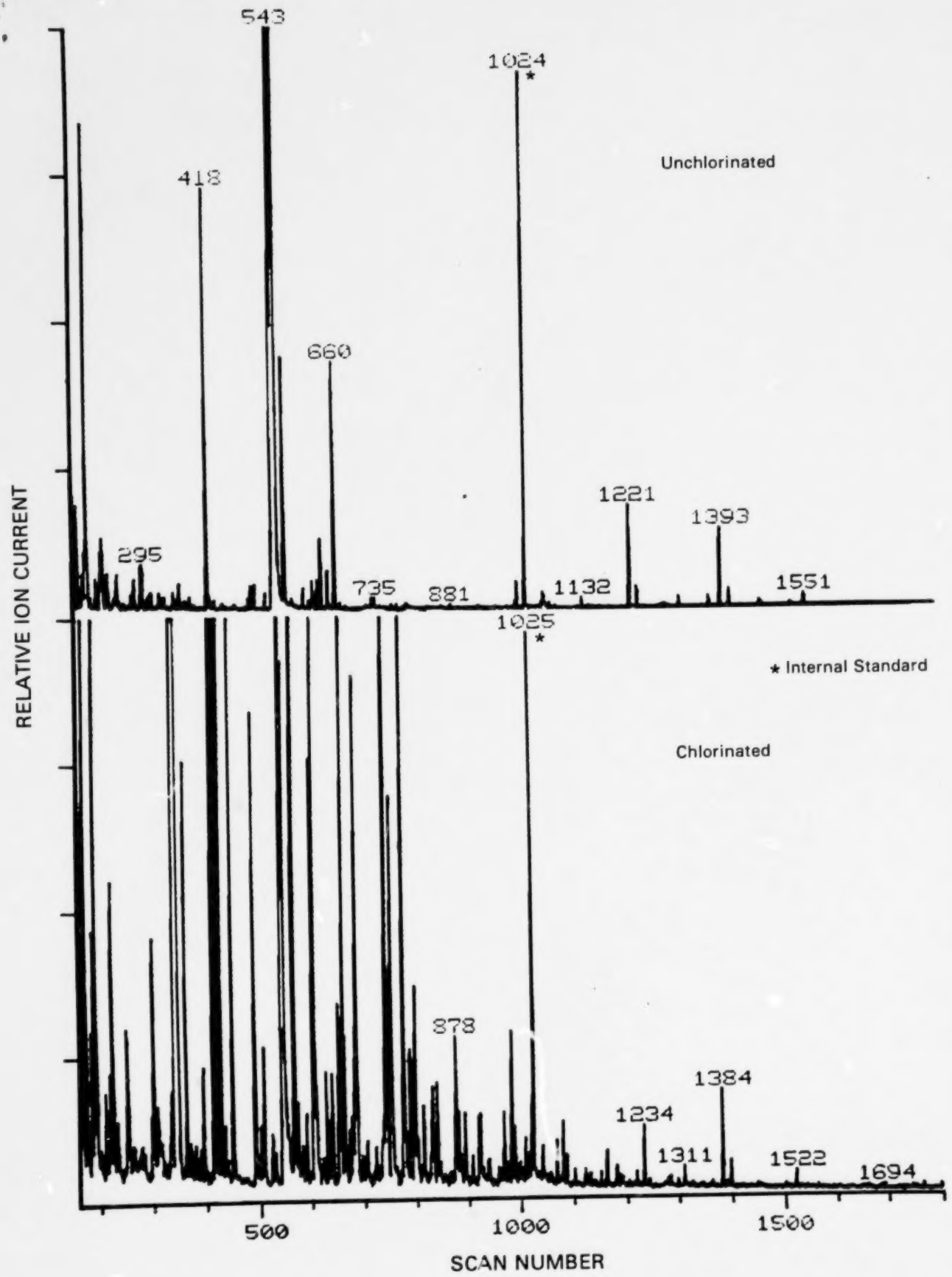

Figure 9. Chlorinated and Unchlorinated Soil Humic Acid Total Ion Current Profiles